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**A Process for the Microbial Leaching of Sulfidic Materials,
and the Use of Sulfur-containing Amino Acids
in Said Microbial Leaching**

Specification

The invention relates to an effective and environmentally safe process for the microbial leaching of sulfidic materials, particularly of sulfide ores such as pyrite, marcasite, chalcopyrite, bornite, or covellite, which process is characterized in that the aqueous leaching fluid is added with sulfur-containing amino acids or derivatives thereof. The invention is also directed to the use of sulfur-containing amino acids or derivatives thereof in the microbial leaching of sulfidic materials, particularly in pyrite leaching.

Microbial leaching is a well-known process in bio-hydrometallurgy for leaching out metals from ores and other mineral raw materials through the action of microorganisms. Obligately chemolithoautotrophic *Thiobacillus* species such as *T. ferrooxidans* and *T. thiooxidans* whose energy sources are sulfides, elemental sulfur and soluble thiosulfates, but also iron(II) ions as an alternative, play a central role in the chemistry of ore leaching. In any case, the microbial action leads up to the sulfate. As an example, reference is made to US 2,829,964 wherein a cyclic leaching process using iron-oxidizing bacteria is described. In this process, the ore is leached with a sulfuric Fe(III) sulfate solution obtained using bacteria. Thereafter, leach and gangue are separated, the leach metal

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content is extracted, and the Fe(II)-containing final leach is re-oxidized using bacteria.

The literature also suggests a number of processes to improve ore leaching and, in particular, to increase the leaching rate, which processes, above all, envisage the use of surface-active substances (D.W. Duncan, P.C. Trussell, and C.C. Walden, Leaching of Chalcopyrite with *Thiobacillus ferrooxidans*: Effect of Surfactants and Shaking, 1964, Applied Microbiology 12(2), 122-126; I. Palencia, F. Carranza, and J. Pereda, Influence of Block Copolymers on the Microbiological Leaching of Pyrites by Discontinuous Operation, 1984, Tenside Detergents 21(2), 90-93; N. Wakao, M. Mishina, Y. Sakurai, and H. Shiota, Bacterial Pyrite Oxidation III. Adsorption of *Thiobacillus ferrooxidans* Cells on Solid Surfaces and Its Effects on Iron Release from Pyrite, 1984, J. Gen. Appl. Microbiol. 30, 63-67).

It is believed that these substances - chiefly surfactants or polysaccharides and peptides or proteins - improve the contact between bacteria and sulfide, thereby facilitating bacterial attack.

However, the surfactants that are used are disadvantageous because they have lacking or low biodegradability and do not represent environmentally safe substances. Peptides and proteins as surface-active compounds exhibit controversial effects in the leaching process.

It was therefore the object of the present invention to provide an effective leaching process with improved dissolution rate without the use of environmentally hazardous additives.

Surprisingly, it has now been found that bacterial attack by *Thiobacillus* species on sulfidic materials can be

greatly accelerated by adding the aqueous leaching fluid with an amino acid, selected from cysteine, methionine, or derivatives thereof, or a mixture of these compounds at low concentration.

More specifically, homocysteine and amides or esters of cysteine, methionine or homocysteine are possible as derivatives which can be used in the leaching process according to the invention. Homocysteine is a derivative of methionine wherein the methyl group on the sulfur has been replaced by hydrogen, so that homocysteine - like cysteine - has a sulfhydryl group. According to the invention, both racemates and optically active forms of the amino acids may find use.

It has been found that an optimum effect is achieved in those cases where the concentration of the added amino acid(s) or derivatives thereof in the aqueous leaching fluid is low, not exceeding 8×10^{-3} M, in particular. Concentrations of from 8×10^{-4} to 8×10^{-5} M are particularly preferred. The pH value of the leaching fluid is adjusted to 1.0-4.0, preferably to 1.5-2.0, and more preferably to 1.6. Adjustment is effected using suitable buffer solutions, e.g. Tuovinen buffer (Arch. Mikrobiol, 88, 285-298 (1973)).

According to the invention, there are two possible ways of performing the leaching process. On the one hand, the leaching fluid may include both the *Thiobacillus* species and the sulfur-containing amino acids or derivatives thereof. This embodiment is the preferred one. Alternatively, it is also possible to use the dilute amino acid solution alone as leaching fluid and subsequently add the thiobacilli to the discharging fluid (e.g. outside the dump) which is recycled. These two possible ways do not exclude the principal methods of ore leaching well-known to

those skilled in the art, i.e., slope leaching, dump leaching or *in situ* leaching. In practice, the process according to the invention can be used with any of the three ore leaching processes.

According to the invention, *T. ferrooxidans* is preferred as *Thiobacillus* species. This strain is acidophilic, occurring in acidic waters of ore mines. Detailed investigations relating to the growth of this strain have also been described by Tuovinen O.H. et al. in Arch. Mikrobiol. 88, 285-298 (1973).

Thus, the process of the invention provides an effective method of ore leaching, particularly of pyrite, which process, in contrast to current methods such as cyanide leaching, does not represent any risk for the ecological balance of the environment. The amino acids and their derivatives used according to the invention are environmentally safe and inexpensive starting materials. They are employed at exceedingly low concentrations and result in an essential improvement of bacterial dissolution of metal sulfides (e.g. FeS₂). Thus, for example, the process according to the invention permits speeding up the microbial recovery of copper or gold from pyrite ores.

The invention is also directed to the novel use of sulfur-containing amino acids, derivatives or mixtures thereof in the microbial leaching of sulfidic materials, particularly of sulfide ores.

With reference to the embodiments, the invention will be illustrated in more detail below.

Emb diments

Example 1:

Preparation of pyrite layers using a low-pressure MOCVD plant (metal-organic chemical vapor deposition)

The metal-organic chemical vapor deposition (MOCVD) is a process for preparing thin polycrystals and epitaxial layers, said layers being deposited from the gaseous phase. Organometallic compounds are mostly used as starting materials (precursors). The deposition process proceeds as follows: A carrier gas is passed through so-called bubblers. The bubbler contains the organometallic compounds in liquid or solid form. As a result, the starting materials are taken up by the carrier gas. The starting compounds are passed over a heated substrate by the carrier gas. The starting compounds include the elements which are to form the layer. The compounds undergo decomposition over the substrate surface in a reaction. As a result, the elements contributing to layer formation are liberated. These elements attach to the substrate surface, thereby forming the layer. Excess decomposition products are conveyed to the vent air by the carrier gas. In the present Example, the pyrite layers are prepared using an MOCVD plant as described in "Solar Energy Materials and Solar Cells" 1993, 29, 289-370. Elemental sulfur was used as suitable sulfur precursor. In the preparation of pyrite, iron pentacarbonyl $[\text{Fe}(\text{CO})_5]$ was used as iron precursor.

Example 2:

*Acceleration of bacterial dissolution of pyrite layers with *Thiobacillus ferrooxidans* in the presence of cysteine*

Each time, 1 cm² of pyrite layers 100 nm in thickness (referred to as S°-FeS₂), prepared according to Example 1 using elemental sulfur as precursor, was added with

300 μ l of aqueous solutions or suspensions of *Thiobacillus ferrooxidans* cells and cysteine at concentrations of from 8×10^{-2} to 8×10^{-5} M in an *in situ* pyrite culture chamber. The pH value of the solutions was adjusted to 1.6 using Tuovinen buffer (for 1 liter: KH_2PO_4 = 0.4 g, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ = 0.4 g, $(\text{NH}_4)_2\text{SO}_4$ = 0.4 g, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ = 33.3 g, with no iron(II) being added) [cf., Tuovinen and Kelly, Arch. Mikrobiol. 88, 285-298 (1973)].

Fig. 1 is a plot of the pyrite corrosion level (or dissolution rate) [%] as a function of time [days] for the various solutions. Clearly, the bacterial pyrite dissolution rate is highly accelerated in the presence of a sulfur-containing amino acid at concentrations below 8×10^{-3} M. At concentrations of 8×10^{-4} M and 8×10^{-5} M cysteine in the solution, a lag phase no longer occurs, and a pyrite corrosion level of 100% is achieved after only 10-11 days.